

19



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

11

Publication number:

**0 353 722  
A2**

12

## EUROPEAN PATENT APPLICATION

21 Application number: 89114222.6

51 Int. Cl.<sup>4</sup>: **C07C 67/36 , C07C 67/37 ,  
C07C 69/14**

22 Date of filing: 01.08.89

30 Priority: 02.08.88 US 227295

43 Date of publication of application:  
07.02.90 Bulletin 90/06

84 Designated Contracting States:  
BE DE ES FR GB IT

71 Applicant: **UNION CARBIDE CHEMICALS AND  
PLASTICS COMPANY INC.** (a New York  
corporation)  
39 Old Ridgebury Road  
Danbury Connecticut 06817-0001(US)

72 Inventor: **Wegman, Richard William**  
912 Glendale Avenue  
South Charleston West Virginia 25303(US)

74 Representative: **Barz, Peter, Dr. et al**  
Patentanwälte Dipl.-Ing. G. Dannenberg Dr.  
P. Weinhold, Dr. D. Gudel Dipl.-Ing. S.  
Schubert, Dr. P. Barz Siegfriedstrasse 8  
D-8000 München 40(DE)

54 **Carbonylation reaction and catalyst therefor.**

57 A process and novel catalyst for the carbonylation of one or more of alcohols, ethers and ether alcohols to esters and, optionally, to carboxylic acids. The reaction is effected in the vapor state over a solid catalyst comprising a polyoxometalate anion in which the metal is at least one taken from Group V and VI of the Periodic Chart of the Elements complexed with a cation from a member of Group VIIA of the Periodic Chart of the Elements. Preferably, the catalyst is deposited on a support that is inert to the reaction. The preferred support is silica.

**EP 0 353 722 A2**

Xerox Copy Centre

supported on silica. Methanol carbonylation is carried out at 150-200 °C. and 1-5 atm CO, and methyl acetate selectivity is high. In these examples, CH<sub>3</sub>I is not utilized in the reaction feed.

Vapor phase processes that need CH<sub>3</sub>I as a promoter will be corrosive and require expensive materials of construction. In addition, extensive separation/purification procedures are required in order to remove iodides from the product.

Heteropoly acids are well known compounds. The name "heteropoly acids" refers to a broad class of compounds of varying composition. A good general review of their physical properties is given by *Tisgdimos* in Climax Molybdenum Company, Bulletin Cdb-12a, 1969.

The use of heteropoly acids in many areas of catalysis is well known including dehydration of alcohols, Friedel-Crafts type reactions, oxidative dehydrogenation and partial oxidation of organic compounds. For examples see Matveev, et. al., *J. Mol. Cat.*, 38, 345, 1986, Dun, et. al., *Applied Catalysis*, 21, 61, 1986, Nomiya, et al., *Bull. Chem. Soc. Jap.*, 53, 3719, 1980, and Izumi, et. al. *J. Mol. Cat.*, 18, 299, 1983. Recently, much attention has been given to heteropoly acids as a catalyst for the conversion of methanol into hydrocarbons:

(4)  $x\text{CH}_3\text{OH} \rightarrow \text{CH}_2=\text{CH}_2 + \text{CH}_3\text{CH}=\text{CH}_2 + \text{other hydrocarbons}$

See *Moffat, et.al., J. of Cat.*, 77, p. 473, 1982, *Ono, et al. Bull. Chem. Soc. Jap.*, 55, p. 2657, 1982, and *Moffat, et.al., J. of Cat.*, 81, p. 61, 1983. This reaction is carried out in the vapor phase (300-375 °C.) and the products include ethylene, propylene and saturated C<sub>1-5</sub> hydrocarbons. Reaction 4 dominates the known chemistry of reactions of methanol in the presence of heteropoly acids. It was therefore unexpected to find that methanol carbonylation could be carried out with heteropoly acids.

Heteropolyacids and polyoxometalate anions constitute well recognized compositions. They embrace the well-known complexes called isopolyoxoanions and heteropolyoxoanions. They are represented by the general formulas<sup>1</sup>

25

$[\text{M}_m\text{O}_y]^{p-}$	Isopolyanions
$[\text{X}_x\text{M}_m\text{O}_y]^{q-}$ ( $x \leq m$ )	Heteropolyanions

30

wherein M is at least one metal taken from Group V and VI of the Periodic Chart of the Elements (such as molybdenum, tungsten, vanadium, niobium, chromium, and tantalum) in their highest (d<sup>0</sup>, d<sup>1</sup>) oxidation states, and X is a heteroatom from all groups of the Period Chart of the Elements with the possible exception of the rare gases.<sup>2</sup>

(1. See Pope, Heteropoly and Isopoly Oxometalates, Published by Springer-Verlag, Berlin, 1983, page 1.)

(2. Pope, supra, page 2, takes the position that the "terms polyoxometalate or or polyoxoanion might be therefore more appropriate to describe the field")

This invention relates to a novel vapor phase carbonylation process of alcohols and ethers which utilizes polyoxometalate anions as the catalysts and to the catalysts. The process involves the carbonylation of one or more of alcohols, ethers, and ether alcohols to esters and, optionally, to carboxylic acids, by reaction thereof in the vapor state over a solid catalyst comprising a polyoxometalate anion in which the metal is at least one taken from Group V and VI of the Periodic Chart of the Elements complexed with a cation from a member of Group VIIIA of the Periodic Chart of the Elements.

The process of the invention, in a preferred embodiment, involves the carbonylation of one or more of alcohols, such as mono- and polyhydric alcohols, alkylethers, such as alkyl or alkylene mono- and polyethers, and alkyl ether alcohols to alkyl alkane monoesters and diesters and, optionally, to alkane monocarboxylic or dicarboxylic acids, by reaction in the vapor state over a solid catalyst comprising a polyoxometalate anion in which the metal is at least one taken from Group V and VI of the Periodic Chart of the Elements (such as molybdenum, tungsten, vanadium, niobium, chromium, and tantalum), complexed with at least one Group VIIIA (of the Periodic Chart of the Elements) cation, such as Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt. Preferably, the catalyst is deposited on a support that is inert to the reaction. The preferred support is silica.

The invention also embraces solid catalysts for the carbonylation of one or more alcohols, ethers and ether alcohols to esters and, optionally, to carboxylic acids, by reaction thereof in the vapor state. The carbonylation catalysts comprise a polyoxometalate anion in which the metal is at least one taken from Group V and VI of the Periodic Chart of the Elements (such as molybdenum, tungsten, vanadium, niobium, chromium, and tantalum), complexed with at least one Group VIIIA (of the Periodic Chart of the Elements)

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$   
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$   
 $\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CHOCH}_3$   
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$   
5  $\text{CH}_3\text{CH}_2\text{CH}(\text{OCH}_3)\text{CH}_2\text{CH}_3$   
 $\text{CH}_3(\text{CH}_3)\text{C}(\text{OCH}_2\text{CH}_3)\text{CH}_2\text{CH}_3$   
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$   
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OCH}_3)\text{CH}_2\text{CH}_3$   
 $\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CHCH}_2\text{CH}_2\text{OCH}_3$   
10  $\text{CH}_3(\text{CH}_3\text{CH}_2)\text{CHCH}_2\text{CH}_2\text{OCH}_3$   
 $\text{CH}_3(\text{CH}_2)_{17}\text{OCH}_3$   
 $\text{C}_6\text{H}_{11}\text{OCH}_3$   
 $\text{C}_6\text{H}_{11}\text{CH}_2\text{OC}_6\text{H}_5$   
 $\text{C}_6\text{H}_5\text{OH}$   
15  $\text{o-C}_6\text{H}_5(\text{CH}_2\text{OCH}_3)_2$   
 $1,2,4\text{-C}_6\text{H}_5(\text{CH}_2\text{OCH}_3)_3$   
 $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$   
 $\text{CH}_3\text{O}(\text{CH}_2)_4\text{-17CH}_2\text{OH}$   
 $\text{sym-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{OH}$   
20  $(\text{CH}_3\text{OCH}_2)_2(\text{HOCH}_2)_2\text{C}$   
 $\text{CH}_3(\text{CH}_3)\text{CHCH}_2\text{OCH}_2\text{CH}_3$   
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OCH}_2\text{CH}_2\text{OCH}_3)\text{CH}_3$   
 $\text{CH}_3\text{CH}_2\text{CH}(\text{OCH}_2\text{CH}_3)\text{CH}_2\text{CH}_3$   
 $\text{CH}_3(\text{CH}_3)\text{CHCH}(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3)\text{CH}_3$   
25  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{OCH}_3)\text{CH}_3$   
 $\text{CH}_3\text{CH}_2\text{CH}_2(\text{CH}_3)\text{CHCH}_2\text{OCH}_3$   
 $\text{CH}_3\text{CH}_2(\text{CH}_3\text{CH}_2)\text{CHCH}_2\text{OCH}_3$   
 $\text{CH}_3(\text{CH}_2)_8\text{OCH}_3$   
 $\text{CH}_3(\text{CH}_2)_8(\text{CH}_3)\text{CH}_2\text{OCH}_3$   
30  $\text{C}_6\text{H}_{11}\text{OC}_6\text{H}_{11}$   
 $\text{C}_6\text{H}_5\text{OCH}_3$   
 $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_3$   
 $\text{p-C}_6\text{H}_5(\text{CH}_2\text{OCH}_3)_2$   
 $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{1-30}\text{OCH}_3$   
35  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$   
 $(\text{CH}_3\text{OCH}_2)_4\text{C}$   
 $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{1-30}\text{OH}$   
 $1,4\text{-CH}_3\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OCH}_3$

The process of the invention involves providing the alcohol and/ether in the vapor state and passing the  
 40 vapor over a bed containing the solid catalyst comprising a polyoxometalate anion in which the metal is at  
 least one taken from Group V and VI of the Periodic Chart of the Elements (such as molybdenum, tungsten,  
 vanadium, niobium, chromium, and tantalum), complexed with at least one Group VIIIA (of the Periodic  
 Chart of the Elements) cation, such as Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt. The temperature at which the  
 reaction is effected is not seen to be narrowly critical. A temperature between about 100° C. and about  
 45 350° C. is usable. Preferably, the temperature of the reaction is between about 125° C. and about 325° C.,  
 and temperatures between about 150° C. and about 300° C. are most preferred.

The reaction pressure accommodates the requirement that the reactants be fed to the reactor in the  
 vapor state. However, the pressure at which the reaction may be carried out may range from about 1  
 atmosphere to about 1,000 atmospheres, with pressures of greater than 1 atmosphere to about 35  
 50 atmosphere being preferred. The particular reactants and the rate of reaction will impact on the pressure of  
 the reaction zone.

The reaction zone is where the catalyst is located. The reaction may be carried out in a tubular reactor  
 using a fixed bed of the catalyst. The reactants may be fed to the catalyst by feeding down or up, or a  
 combination of both, to a fixed bed located in an upright tubular reactor. It is preferred to use a reactor  
 55 design that operates by plug flow and causes the minimal turbulence in the reaction zone. The reaction  
 may be effected in a dynamic bed of the catalyst. In such a reaction, the bed of catalyst is moving such as  
 in the case of a fluid bed of the catalyst.

The gas hourly space velocity<sup>3</sup> of the reactants through the reaction zone may be over a broad range.

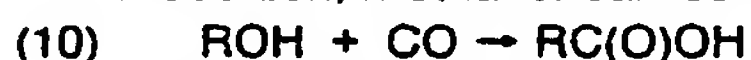
at least about 100 square meters per gram determined by the BET method. In the preferred embodiment of the invention, the surface area of the support onto which the heteropoly acid is deposited, and in contact with, has a surface area of at least about 200 square meter per gram, most preferably at least about 250 square meter per gram. Typical support materials suitable for the invention are the silicas, the gamma-aluminas, the titanias, the alumina silicates, the high surface area clays, and the like. Particularly desirable are the mixed composite supports in which the high surface area support is deposited over a lower surface area support. For example, a silica gel deposited and cured on the surface of an alpha-alumina provides the high surface area for the subsequent deposition of the heteropoly acid onto the silica gel coating and the thermal stability provided by the low surface area alpha-alumina.

The impregnation step simply involves the coating of the support with the heteropoly acid and then drying the coating on the support to fix it. The drying temperature is not narrowly critical and can range from about 100°C. to about 600°C. for a period of about 5 seconds to about 8 hours. The lower the temperature, the longer will be the heating period and the higher the temperature, the shorter will be the heating period.

The most commercially interesting reactants are methanol and dimethyl ether. The products are methyl acetate and acetic acid. The methyl acetate selectivity can be at least 95% at 225°C. and 1 atm total operating pressure.



In addition, methanol can be carbonylated to acetic acid as shown in Equation 10, below.



In the case of the carbonylation of methanol, dehydration occurs as a side reaction due to the acidic nature of the heteropoly acid catalysts of the invention, e. g., the  $\text{M}[\text{W}_{12}\text{PO}_{40}]$  catalysts. Dehydration results in the formation of dimethyl ether as shown by equation 11.



Since dimethyl ether is carbonylated to methyl acetate (equation 6) it can be recycled back to the reactor with no loss in methanol efficiency. Thus, the feed to the reactor can comprise methanol, dimethyl ether or a combination of both.

In the examples which follow, the GHSV = 900 hr<sup>-1</sup> and the LHSV = 0.15 hr<sup>-1</sup>. The reactor was a clean 1/4" stainless steel tube packed with glass wool, 2 milliliter of catalyst and additional glass wool. The tube was placed in an aluminum block surrounded by a heater and connected to the feed and exit lines. The CO flow was started, the temperature of the feed/exit lines adjusted to 160°C. and the reactor taken to the desired temperature. At temperature the methanol feed was started and the system was allowed to equilibrate 0.5 hr. Each experiment was normally carried out for 6 hr. The gas stream exiting the reactor was analyzed with a HP 5830 gas chromatograph equipped with a TC detector and a 10' x 1/8" column packed with Poropak Super Q. The following program was used: temp 1 = 50°C., time 1 = 0 min., rate = 15 degrees/min., temp 2 = 225°C., time 2 = 20 min.

#### Examples 1-9

The various  $\text{MW}_{12}\text{PO}_{40}/\text{SiO}_2$  compounds listed in Table 1 below were prepared on a silica support having a surface area of about 683 m<sup>2</sup>/gram according to the procedure described above and examined as catalysts for the carbonylation of methanol. The experiments were carried out at 225°C. and 1 atm. with LHSV = 0.15 hr<sup>-1</sup> and GHSV = 900 hr<sup>-1</sup>. The results are listed in Table 1. The reported catalyst compositions are idealized stoichiometries.

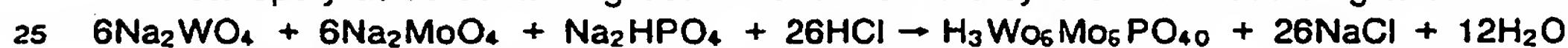
In these example,  $\text{Na}_3[\text{Rh}_2\text{W}_{12}\text{O}_{42}]$  without deposition on silica support (catalyst "A") and deposited on silica support (catalyst "B") were examined as carbonylation catalysts. The runs were carried out similar to Example 1-9. The results are reported in Table 3 below.

Table 3

Ex. No.	Catalyst	Temp. °C.	Product Yield		
			MeOH	DME	MeOAc
19	A	225	99.0	0.0	1.0
20	A	250	98.0	0.0	2.0
21	A	275	96.0	0.0	4.0
22	B	225	87.0	0.0	13.0
23	B	275	85	0.0	15.0

## Examples 24-27

Heteropoly acids containing both W and Mo were synthesized according to the following reaction:



The reaction is general therefore  $\text{H}_3\text{W}_x\text{Mo}_y\text{PO}_{40}$ , where  $x + y = 12$ , were prepared by adjusting the ratios of the reagents. The  $\text{H}_3\text{W}_x\text{Mo}_y\text{PO}_{40}$  acids were then exchanged with Rh and deposited onto  $\text{SiO}_2$  to give  $\text{RhW}_x\text{Mo}_y\text{PO}_{40}/\text{SiO}_2$  catalysts. The catalysts were examined at 225 °C, 1 atm CO and GHSV = 900  $\text{hr}^{-1}$ . The results are given in Table 4 below.

Table 4

Catalyst			
$\text{RhW}_x\text{Mo}_y\text{PO}_{40}$			
Example No.	x	y	MeOAc Yield %
24	8	4	16.0
25	6	6	11.0
26	4	8	8.0
27	2	10	4.0

## Examples 28-33

In these examples methanol was replaced by dimethyl ether. The reaction was carried out at 225 °C. and 1 atm. CO with the catalysts reported in Table 5 below. Each of the catalysts were deposited and supported on high surface area silica, as characterized above.

HPdW<sub>12</sub>PO<sub>40</sub>, HMnW<sub>12</sub>PO<sub>40</sub>, HCoW<sub>12</sub>PO<sub>40</sub>, HNiW<sub>12</sub>PO<sub>40</sub>, FeW<sub>12</sub>PO<sub>40</sub>, HZnW<sub>12</sub>PO<sub>40</sub>, ThW<sub>12</sub>PO<sub>40</sub>, Na<sub>8</sub>-[Rh<sub>2</sub>W<sub>12</sub>O<sub>42</sub>], Ir-Pd[W<sub>12</sub>PO<sub>40</sub>], and Rh-Pd[W<sub>12</sub>PO<sub>40</sub>].

15. The catalyst of claim 11 derived from RhW<sub>x</sub>Mo<sub>y</sub>PO<sub>40</sub> wherein x and y are the following combinations:

x	y
8	4
6	6
4	8
2	10

16. The catalyst of any of claims 11 to 15 deposited on a solid support.



(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 353 722 A3**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **89114222.6**

(51) Int. Cl.<sup>5</sup>: **C07C 67/36, C07C 67/37,  
C07C 69/14**

(22) Date of filing: **01.08.89**

(30) Priority: **02.08.88 US 227295**

(43) Date of publication of application:  
**07.02.90 Bulletin 90/06**

(84) Designated Contracting States:  
**BE DE ES FR GB IT**

(88) Date of deferred publication of the search report:  
**31.07.91 Bulletin 91/31**

(71) Applicant: **UNION CARBIDE CHEMICALS AND  
PLASTICS COMPANY INC. (a New York  
corporation)  
39 Old Ridgebury Road  
Danbury Connecticut 06817-0001(US)**

(72) Inventor: **Wegman, Richard William  
912 Glendale Avenue  
South Charleston West Virginia 25303(US)**

(74) Representative: **Barz, Peter, Dr. et al  
Patentanwälte Dipl.-Ing. G. Dannenberg Dr.  
P. Weinhold, Dr. D. Gudel Dipl.-Ing. S.  
Schubert, Dr. P. Barz Siegfriedstrasse 8  
W-8000 München 40(DE)**

(54) **Carbonylation reaction and catalyst therefor.**

(57) A process and novel catalyst for the carbonylation of one or more of alcohols, ethers and ether alcohols to esters and, optionally, to carboxylic acids. The reaction is effected in the vapor state over a solid catalyst comprising a polyoxometalate anion in which the metal is at least one taken from Group V and VI of the Periodic Chart of the Elements complexed with a cation from a member of Group VIIIA of the Periodic Chart of the Elements. Preferably, the catalyst is deposited on a support that is inert to the reaction. The preferred support is silica.

**EP 0 353 722 A3**